PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-159522

(43)Date of publication of application : 13.06.2000

(51)Int.Cl. C01G 45/00
C01G 49/00
H01M 4/58
H01M 10/40

(21)Application number : 10-329536

(22)Date of filing : 19.11.1998

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(54) MAGNESIUM-INCLUDING LITHIUM-MANGANESE COMPOUND OXIDE HAVING SPINEL STRUCTURE, AND PRODUCTION AND USE OF THE SAME COMPOUND OXIDE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium-manganese compound oxide having a spinel structure, in which the elution of Mn is restrained in an organic electrolyte solution, and also to provide a lithium secondary battery excellent in cycle stability.

SOLUTION: This magnesium-including lithium-manganese compound oxide having a spinel structure is expressed by the formula Lix.Mgy1.My2.Mn(2-y1-y2)O4 [wherein, M is Cr, Fe, Ti, Al or the like; $1<(x)\leq 1.15$; $0.01\leq(y1)\leq 0.2$; $0\leq y2\leq 0.2$], and has 0.2-7 μm average primary particle diameter and 0.05-2 m2/g BET specific surface area. When producing the magnesium-including lithium-manganese compound oxide having a spinel structure by blending a Li compound and a Mn one with a Mg compound and by calcinating the mixture, the calcination temperature is 800-950°C. The magnesium-including lithium- manganese compound oxide having a spinel structure is adopted in a Li secondary battery as an anode active material.

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CLAIMS

[Claim(s)]
[Claim 1] A formula Lix-Mgy1-My2-Mn(2-y1-y2) O Mg content Spinel structure lithium manganese multiple oxide characterized by being expressed with 4 (however, these M elements 1< x<=1.15, 0.01<=y, such as Cr, Fe, Ti, and aluminum 1<=0.2, 0<=y 2<=0.2), for the first [an average of] particle diameter being 0.2-7 micrometers, and a BET specific surface area being 0.05-2m2/g.
[Claim 2] Mg content Spinel structure lithium manganese multiple oxide characterized by being y2=0 in a formula, and being expressed with formula Lix-Mgy1 and Mn(2-y1) O4 (however, 1< x<=1.15, 0.01<=y<=0.2), for the first [an average of] particle diameter being 0.2-7 micrometers, and a BET specific surface area being 0.05-2m2/g in Mg content Spinel structure lithium manganese multiple oxide according to claim 1.
[Claim 3] A manufacture method of claim 1 characterized by burning temperature being 800-950 degrees C in a manufacture method of Li compound, Mn compound, and Mg content Spinel structure lithium manganese multiple oxide that mixes Mg compound and is calcinated, and Mg content Spinel structure lithium manganese multiple oxide according to claim 2.
[Claim 4] Li rechargeable battery characterized by using Mg content Spinel structure lithium manganese multiple oxide according to claim 1 or 2 as positive active material in Li rechargeable battery which consists of nonaqueous electrolyte and a separator which dissolved a positive electrode, a negative electrode, and an electrolyte containing Li.
[Claim 5] Li rechargeable battery characterized by using a carbon system material as a negative-electrode active material in Li rechargeable battery of claim 4.

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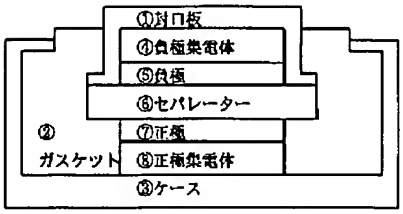
Drawing selection drawing 1



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] This invention relates to a use at Mg content Spinel structure lithium manganese multiple oxide and its manufacture method list.
[0002] The lithium manganese multiple oxide attracts attention in recent years as positive active material for lithium secondary batteries which can attain high power and high energy density.
[0003]
[Description of the Prior Art] As a positive-electrode material for lithium secondary batteries, it is called for that a voltage operating space is high, that it is high discharge capacity, and that cycle stability is high, and the multiple oxide of **s, such as Li and various metals, for example, Co, nickel, Mn, etc., is examined.
[0004] Since the manganese of a raw material is abundant cheaply and in resource and composition is also comparatively easier still manganese, a manganese multiple oxide is a material most expected also in the positive-electrode material for lithium secondary batteries.
[0005] If LiMn 2O4 of the Spinel structure which is a kind of the multiple oxide of Li and Mn can show the two-step discharge which is for a flat part to the 4V neighborhood and the 3V neighborhood and can be made they to carry out a cycle reversibly in the operating space of the 4V neighborhood at the time of discharge, taking out high energy is expected and it is promising as positive active material.
[0006] However, it is supposed that the problem of cycle stability that charge-and-discharge capacity falls will be pointed out if charge and discharge are repeated, and a problem is in especially hot cycle stability.
[0007] On the other hand, if charge and discharge are performed in recent years, using LiMn 2O4 as positive active material for lithium secondary batteries, the phenomenon in which Mn is eluted in an organic electrolyte solution is pointed out.
[0008] Furthermore, this invention person etc. added the organic electrolyte solution to 2OLiMn4 powder, it saved at 85 degrees C, and the place and a lot of Mn which analyzed Mn in an organic electrolyte solution were detected.
[0009] This shows a possibility of stopping operating as a positive electrode for lithium secondary batteries, by the mothball, even if it does not perform charge and discharge, when such LiMn 2O4 is used for the positive-electrode material for lithium secondary batteries.
[0010]
[Problem(s) to be Solved by the Invention] This invention offers the Spinel structure lithium manganese multiple oxide with which Mn elution in the inside of an organic electrolyte solution was controlled, and the lithium secondary battery excellent in cycle stability.
[0011]
[Means for Solving the Problem] As a result of this invention person's etc. inquiring

wholeheartedly paying attention to control of Mn elution, burning temperature is 800-950 degrees C. Formula Lix-Mgy1-My2-Mn(2-y1-y2) O 4 However, this M element is expressed with 1< x<=1.15, such as Cr, Fe, Ti, and aluminum, 0.01 <=y1 <=0.2, and 0 <=y2 <=0.2). (-- Mg content Spinel structure lithium manganese multiple oxide presentation characterized by for the first [an average of] particle diameter being 0.2-7 micrometers, and a BET specific surface area being 0.05-2m2/g comes to complete a header and this invention for the ability of the purpose of this invention to be attained.
[0012]
[Function] Hereafter, this invention is explained to details.
[0013] In the Spinel structure lithium manganese multiple oxide of this invention, it is indispensable to contain Mg.
[0014] The presentation of Mg content Spinel structure lithium manganese multiple oxide of this invention Formula Lix-Mgy1-My2-Mn(2-y1-y2) O 4 However, this M element is expressed with 1< x<=1.15, such as Cr, Fe, Ti, and aluminum, 0.01 <=y1 <=0.2, and 0 <=y2 <=0.2). (-- It is Mg content Spinel structure lithium manganese multiple oxide characterized by for the first [an average of] particle diameter being 0.2-7 micrometers, and a BET specific surface area being 0.05-2m2/g. Formula Lix-Mgy1 and Mn(2-y1) O4 which is y2=0 in a formula especially It may be expressed with (1< x<=1.15, 0.01 <=y1 <=0.2), the first [an average of] particle diameter may be 0.2-7 micrometers, and Mg content Spinel structure lithium manganese multiple oxide characterized by a BET specific surface area being 0.05-2m2/g is sufficient. [however,]
[0015] The amount x of Li(s) is 1< x<=1.15. Mn elution volume to one or less field joint-right machine electrolytic solution increases, and if 1.15 is exceeded, charge-and-discharge capacity will become small.
[0016] The amount y1 of Mg is 0.01<=y<=0.2. Mn elution volume to one or less field joint-right machine electrolytic solution increases, and if 1.15 is exceeded, charge-and-discharge capacity will become small.
[0017] This M yuan quantum y2 is 0.2 or less. If 0.2 is exceeded, charge-and-discharge capacity will become small.
[0018] Here, especially as an M element, although it does not limit, Cr, Fe, Ti, and aluminum are desirable.
[0019] The first [an average of] particle diameter is 0.2-7 micrometers, and the BET specific surface area of Mg content Spinel structure lithium manganese multiple oxide of this invention is 0.05-2m2/g.
[0020] When Mn tends to be eluted in less than 0.2 micrometers, the first [an average of] particle diameter exceeded 7 micrometers on the other hand and it uses it for a cell active material, the high engine performance is hard to be obtained. In addition, the first [an average of] particle diameter said here is observed by SEM.
[0021] When a BET specific surface area uses it for a cell active material under by 0.05m2/g, if 2m2/g is exceeded, on the other hand, Mn will tend to be eluted that the high engine performance is hard to be obtained.
[0022] Mg content Spinel structure lithium manganese multiple oxide of this invention can be manufactured by mixing and calcinating content variety element compounds, such as a manganese compound, a lithium compound, and a magnesium compound.
[0023] Be [what is necessary / just although a compound generates an oxide below with burning temperature in an oxide, a hydroxide, a carbonate, a nitrate, etc.], an oxide, a hydroxide, and its carbonate are especially desirable from the effect which it has on environment.
[0024] The burning temperature in this invention must be 800-950 degrees C.
[0025] In the case of less than 800 degrees C, it is in the orientation for Mn elution volume to

increase and is not desirable. On the other hand, when 950 degrees C is exceeded, if it uses for a cell active material, it **** a bad influence for the engine performance and is not desirable.

[0026] In this invention, Li rechargeable battery which was excellent in cycle stability can be obtained, using Mg content Spinel structure lithium manganese multiple oxide obtained by this invention as positive active material.
[0027] The material which can occlusion emit a lithium or a lithium ion can be used for the negative-electrode active material used with the lithium secondary battery of this invention at a metal lithium list. For example, a metal lithium, a lithium / aluminium alloy, a lithium / tin alloy, a lithium/lead alloy, and the carbon system material electrochemically inserted and desorbed from a lithium ion are suitable especially from the field of safety and the property of a cell.
[0028] Moreover, as an electrolyte used with the lithium secondary battery of this invention, although there is especially no limit, it can use what dissolved lithium salt, and the solid electrolyte of lithium ion conductivity into organic solvents, such as carbonate, sulfolanes, lactone, and ether, for example.
[0029]
[Example] Hereafter, although an example describes this invention concretely, this invention is not limited to this.
[0030] In example 1 type Lix-Mgy1 and Mn(2-y1) O4, after the amount x of Li(s) carried out weighing capacity of MnO2, Li2CO3, and the Mg(OH)2 powder so that 0.1 and the amount of Mn might be set to 1.9 by 1.08 and the amount y1 of Mg, and it was mixed with the mortar, it calcinated at 800 degrees C for 6 hours.
[0031] By SEM, the first [an average of] particle diameter of the obtained powder was measured, and specific surface area was measured with the BET adsorption method.
[0032] Evaluation of Mn elution and evaluation of a cell property were performed by the following method.
[0033] After sinking into 15ml of electrolytic solutions which dissolved the 6 phosphorus-fluoride acid lithium in the mixed solvent of ethylene carbonate and dimethyl carbonate by the concentration of one mol / dm3 and holding 3g of 85 degrees C of "evaluation of Mn elution" sample powder for 50 hours, solid liquid separation was carried out and Mn concentration in the electrolytic solution was analyzed by ICP spectroscopy.
[0034] "Evaluation of cell property" cell trial was carried out using the coin mold cell shown in drawing 1 .
[0035] In the positive electrode, obtained Mg content Spinel structure lithium manganese multiple oxide powder, the polytetrafluoroethylene of an electric conduction agent, and the mixture (trade name: TAB-2) of acetylene black were mixed at a rate of 2:1 by the weight ratio. The pellet obtained by carrying out reduced pressure drying of it at 200 degrees C for 24 hours after fabricating mixture by the pressure of 1 ton/cm2 on a mesh (SUS316) at a pellet type was used.
[0036] Used the obtained pellet for the positive electrode of ** of the cell shown by drawing 1 , used the graphite (trade name: MCMB) electrochemically inserted and desorbed from a lithium ion for the negative electrode of ** of drawing 1 , the separator of ** of drawing 1 was made to carry out impregnation of the solution which dissolved the 6 phosphorus-fluoride acid lithium in the mixed solvent of propylene carbonate and diethyl carbonate by the concentration of one mol / dm3 to the electrolytic solution, and the cell was constituted.
[0037] As for the cell, cell voltage measured a repeat, initial capacity, and a capacity maintenance factor (% of the charge capacity of 50 cycle eye to 10 cycle eye) for charge and discharge between 4.5V and 3.5V with the fixed current of 1.0 mA/cm2.
[0038] Each obtained measured value was shown in a table 1.
[0039] Except that example 2 burning temperature was 900 degrees C, it carried out on the

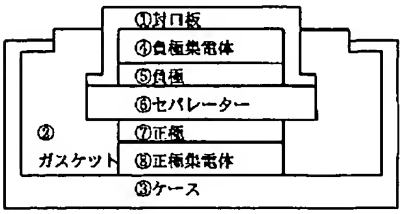
same conditions as an example 1.
[0040] Except that the amount y1 of example 3Mg was 0.02, it carried out on the same conditions as example .2.
[0041] In example 4 type Lix-Mgy1, My2, and Mn(2-y1-y2) O4, these M elements are Cr(s) (y2 is 0.1), for the amount x of Li(s), 1.08 and the amount y1 of Mg were [0.02 and the amount of Mn] 1.88, and except that burning temperature was 800 degrees C, it carried out on the same conditions as an example 3. In addition, Cr 2O3 was used for Cr compound.
[0042] Except that example 5 burning temperature was 900 degrees C, it carried out on the same conditions as an example 4.
[0043] It carried out on the same conditions as an example 1 except not adding an example of comparison 1Mg element.
[0044] Except that example of comparison 2 burning temperature was 700 degrees C, it carried out on the same conditions as an example 1.
[0045] Except that example of comparison 3 burning temperature was 970 degrees C, it carried out on the same conditions as an example 1.
[0046]
[A table 1]

	化学組成	焼成温度 (℃)	平均粒径 (μm)	BET値 (m^2／g)	Mn溶出量 (ppm)	電池容量 (mAH／g)	維持率 (%)
実施例1	Li1.08Mg0.1Mn1.9O4	800	0.5	1.5	0.05	105	98
実施例2	Li1.08Mg0.1Mn1.9O4	900	3	0.3	0.01	100	98
実施例3	Li1.08Mg0.02Mn1.98O4	900	2	0.5	0.01	105	98
実施例4	Li1.08Mg0.02Cr0.1Mn1.88O4	800	0.5	1.7	0.1	107	99
実施例5	Li1.08Mg0.02Cr0.1Mn1.88O4	900	2	0.8	0.05	107	99
比較例1	Li1.08Mn2.0O4	800	0.3	1.6	0.6	105	95
比較例2	Li1.08Mg0.1Mn1.9O4	700	0.1	3.5	0.8	——	——
比較例3	Li1.08Mg0.1Mn1.9O4	970	8	0.2	0.01	65	——

[0047]
[Effect of the Invention] There is little Mn elution in an organic solvent, and even if Mg content Spinel structure lithium manganese multiple oxide of this invention demonstrates the charge-and-discharge cycle nature stabilized by even after the mothball and performs charge and discharge at an elevated temperature further, there is little deterioration.

[Translation done.]

Drawing selection drawing 1



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